Ru L_3-edge XANES as a Probe of Ru Oxidation State

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Beamline(s): **X19A**

Introduction: XANES is a powerful method for determining the oxidation state of an element. This is especially true for catalysts where the active form of the catalyst under reaction conditions could be very different from that when the reactants and products are not present. Recently, we have investigated using XANES at the Ru L_3-edge as a method to probe the oxidation state of Ru under reaction conditions for a series of Ru-based catalysts. While the K-edge of Ru has been studied there has not been much data published of the Ru L-edge of Ru compounds.

Methods and Materials: Ru L_3-edge XANES data were collected on X19A. The data on the high purity bulk compounds was obtained using total electron yield from powders dispersed on tape. The data from the catalysts was obtained in fluorescence yield mode using the PIPS detector.

Results: Fig. 1 shows a comparison of the Ru L_3-edge XANES of Ru metal and RuO_2. The white line of the metal shows a single peak, while that of the oxide shows a shoulder and peak. A shift in the white line maximum of 2.4 eV is measured between Ru^0 and Ru^{4+}. The transition involved in Ru L_3-edge XANES is 2p to 4d. In RuO_2 the Ru ion is in essentially octahedral coordination, and thus experiences a crystal field of O_n symmetry resulting in a splitting of the 4d states into t_{2g} and e_g levels. It is this crystal field splitting that results in the two peaks observed for RuO_2. Thus, in addition to simple oxidation state determination, information about the local geometry around the Ru atom can be determined from L_3-edge XANES. Fig. 2 shows Ru L_3-edge XANES data from a Ru/Al_2O_3 catalyst. The left panel compares the data from an as-received catalyst, and after reduction in situ. The reduction of the Ru from Ru(IV) to Ru(0) is clearly observed. The right hand panel shows the effect of subsequent air exposure for only a few minutes. The reduced Ru quickly re-oxidizes to Ru(IV).

Conclusions: Ru L_3-edge XANES is sensitive to both the oxidation state and the local geometry of the Ru. Data have been collected in situ on a series of Ru/Al_2O_3 catalysts and information about the reducibility of these materials determined.

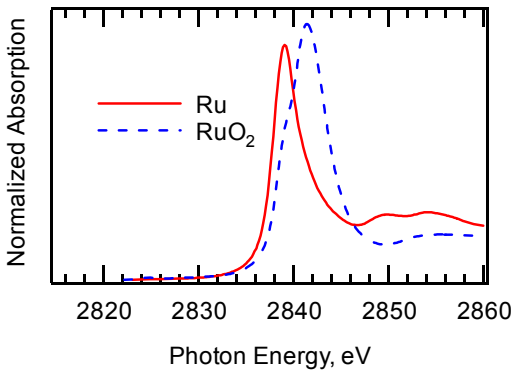

Figure 1. Ru L_3-edge XANES of Ru metal and ruthenium(IV) oxide

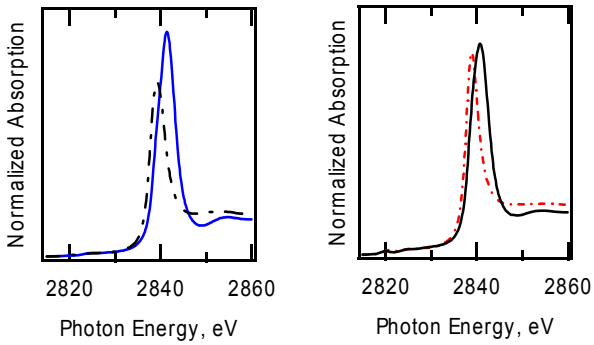

Figure 2. Ru L_3-edge XANES of: Left panel: as-received catalyst (dashed) and after in situ reduction (solid line). Right panel: after reduction (dotted) and after air exposure (solid).